

# Oxidation of lower alkenes by $\alpha$ -oxygen ( $\text{Fe}^{\text{III}}-\text{O}^{\bullet-}$ ) $_{\alpha}$ on the FeZSM-5 surface: The epoxidation or the allylic oxidation?



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## ABSTRACT

Reactions of anion-radical  $\alpha$ -oxygen ( $\text{Fe}^{\text{III}}-\text{O}^{\bullet-}$ ) $_{\alpha}$  with propylene and 1-butene on sodium-modified FeZSM-5 zeolites were studied in the temperature range from  $-60$  to  $25$  °C. Products were extracted from the zeolite surface and identified. It was found that main reaction pathway was the epoxides formation. Selectivity for epoxides at  $-60$  °C was 59–64%. Other products were formed as a result of secondary transformations of epoxides on the zeolite surface. According to IR spectroscopy, the oxidation of propylene over the entire temperature range and 1-butene at  $-60$  °C were not accompanied by the formation of ( $\text{Fe}^{\text{III}}-\text{OH}$ ) $_{\alpha}$  groups, in distinction to methane oxidation. This testifies that hydrogen abstraction does not occur. In case of 1-butene reaction with  $\alpha$ -oxygen at  $25$  °C, hydrogen abstraction occurred but was insignificant, ca 7%. According to DFT calculation ferraooxetane intermediate formation is preferable over hydrogen abstraction. Following decomposition of this intermediate leads to the propylene oxide (PO) formation. The results may be relevant to the low selectivity problem of the silver catalyst in propylene epoxidation and raise doubts about the presently accepted mechanism explaining an adverse effect of allylic hydrogen.

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## 1. Introduction

Selective partial oxidation of hydrocarbons is the most important and challenging task of modern oxidative catalysis [1–6]. In this area, selective epoxidation of alkenes takes a special place. The most important processes here are epoxidation of ethylene and propylene ( $\sim 27$  and 7 million tons per year, respectively) [1,7–10]. Despite the related nature of these processes, in practice they are implemented in essentially different ways. Direct gas-phase epoxidation of ethylene by molecular oxygen proceeds very effectively over supported Ag catalysts and is currently one of the most advanced chemical technologies. However, it is not possible to carry out the epoxidation of propylene in this way due to the significant contribution of its complete oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [1,9,10]. Therefore, to perform the PO synthesis, more complex and less efficient processes should be used.

Nearly a half of PO is currently produced by the well-known chlorohydrin process [8–10]. Essential drawbacks of this process

are the use of molecular chlorine and the formation of toxic Cl-containing by-products. More advanced methods for PO production include the oxidation of propylene by alkyl hydroperoxides (ethylbenzene, *tert*-butane, cumene) and  $\text{H}_2\text{O}_2$ . Among drawbacks of these processes is the necessity of preliminary synthesis of hydroperoxides, their combustibility, and explosibility as well as the formation of considerable amounts of the corresponding alcohols as by-products, which are not always marketable [8–10]. In addition, all the listed processes comprise two steps and are performed in the liquid phase.

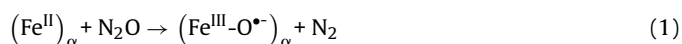
It took two decades to bring some improvements by an intense search for the advanced catalysts and oxidants capable of efficiently performing gas-phase epoxidation of propylene. In particular, promising results were obtained for Au-containing titanosilicates with  $\text{H}_2 + \text{O}_2$  [11–13] and  $\text{CO} + \text{O}_2$  mixtures as the oxidants [14,15]. A rather high PO selectivity was obtained in the oxidation of propylene by  $\text{N}_2\text{O}$  over Fe-containing catalysts [16–21]. Interesting results were published for the propylene epoxidation by oxygen using Cu and Mo-containing systems [22–24]. However, in all cases, the attained conversions and selectivity were still too low for the practical application.

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The failure of attempts to create new catalytic systems has led to a renewed interest in classic silver catalysts in order to understand the cause of their poor selectivity in the epoxidation of propylene and other alkenes [25,26]. Now it is generally accepted that this is due to the presence of weakly bound allylic hydrogen in these alkenes. Therefore, the active electrophilic oxygen species generated on the Ag surface [1,8,10,27] do not attack the C=C olefin bond, as in the case of ethylene, but mainly abstract the allylic hydrogen that leads to complete oxidation [7–9]. However, this hypothesis has no direct experimental evidence. For example, the primary product of propylene reaction with electrophilic oxygen was not identified. There may also be other explanations. Namely, one can assume that in all cases the C=C bond is preferably attacked, but the presence of allylic hydrogen stimulates rapid secondary transformations of the formed epoxides.

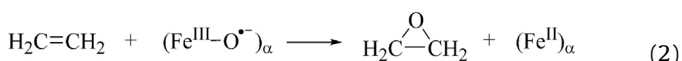
A convenient model of electrophilic oxygen can be represented by the so-called  $\alpha$ -oxygen in the oxyl complex  $(\text{Fe}^{\text{III}}-\text{O}^{\bullet-})_{\alpha}$  [28–33]. A high concentration of such complexes (up to 100  $\mu\text{mol/g}$ ) can be obtained by decomposition of  $\text{N}_2\text{O}$  over FeZSM-5 and some other Fe-containing zeolites [28–30,34–36]:



This is by three orders of magnitude higher as compared to the concentration of  $\text{O}^{\bullet-}$  on conventional oxide catalysts [37,38]. In addition,  $\alpha$ -oxygen is highly stable in an inert atmosphere (up to 250 °C) and chemically homogeneous [28,29,39]. These features make FeZSM-5 zeolites a unique model system allowing the mechanistic studies to be performed at a quantitative level that was impossible on other catalysts.

FeZSM-5 zeolite was used to investigate the oxidation mechanisms for some model reactions. It was shown that  $\text{O}_{\alpha}$ , similar to oxygen radicals  $\text{O}^{\bullet-}$ , has a very high ability to abstract the hydrogen atom. Already at room temperature,  $\alpha$ -oxygen stoichiometrically reacts with methane [35,40–42], hydrogen [39] and even water [43–45] to produce hydroxyl complexes  $(\text{Fe}^{\text{III}}-\text{OH})_{\alpha}$ . At higher temperatures, methane oxidation proceeds in the catalytic mode to yield methanol as the primary product [42,46,47].

Recently, we investigated the stoichiometric oxidation of ethylene by  $\alpha$ -oxygen, which showed that the reaction leads to  $\text{O}_{\alpha}$  addition over the C=C double bond, yielding ethylene oxide as the primary product [48]:



The present work is a continuation of the previous study and is devoted to the oxidation of propylene and 1-butene by  $\alpha$ -oxygen. The main goal of the work is to identify the primary products of these interactions and reveal which of the processes – epoxidation or allylic oxidation – is the main route of the reaction with  $\text{O}_{\alpha}$ . The answer to this question would be of fundamental importance for evaluating the potential of Ag as an effective catalyst for the epoxidation of not only ethylene but also other lower alkenes.

## 2. Experimental

### 2.1. Materials

The initial sample was ZSM-5 zeolite grade CBV2314 (Zeolyst Corp., Si/Al = 11.5,  $\text{C}_{\text{Na}} < 0.04$  wt.%); 2.0 wt.% of iron was introduced into the zeolite by incipient wetness impregnation with a  $\text{FeCl}_3$  solution. To provide an increased concentration of  $\alpha$ -sites, after heating at 550 °C in air the sample was activated by calcination in vacuum at 900 °C (denoted as FeZSM-5). This zeolite is similar to the zeolite employed in recent studies of the  $\text{CH}_4 + \text{O}_{\alpha}$  reaction [40,42].

In order to decrease the acidity, the sample was then modified with sodium (0.2 and 0.4 wt.%). The zeolite was impregnated with a  $\text{NaNO}_3$  solution (0.1 M and 1 M, respectively), followed by drying and calcination at 550 °C. The resulting samples are denoted as 0.2Na-FeZSM-5 and 0.4Na-FeZSM-5. High crystallinity of the zeolite as well as the absence of foreign phases are evidenced by XRD data collected both before and after its activation.

High purity nitrous oxide (medical quality), propylene and 1-butene (polymerization quality) were used in the work. Products formed in the reaction were identified using witness standards purchased from Sigma-Aldrich: PO, propanal (PA), allyl alcohol (AA), *cis*- and *trans*-2,5-dimethyltetrahydrofuranes (DMTHF), 2-methylpentanal, 4-methyl-2-pentanone, 2-hexanone, 1,2-butylene oxide, butyraldehyde, and 2-butanone.

### 2.2. Deposition of $\text{O}_{\alpha}$ and its reactions

The deposition of  $\alpha$ -oxygen and its reaction with propylene and 1-butene were carried out in a static vacuum setup ( $10^{-7}$  Torr) described in detail elsewhere [43]. The setup was equipped with absolute pressure gauges (0.002–100 Torr) and a mass spectrometer PPT Residual Gas Analyzer (MKS Instruments). A zeolite sample (0.1 g) was loaded into a quartz microreactor ( $6.5 \text{ cm}^3$ ), which can easily be isolated from the rest reaction volume of  $720 \text{ cm}^3$  capacity. The sample was subjected to a standard pretreatment that included alternate heating at 550 °C in vacuum and in oxygen at 2 Torr pressure. Such pretreatment provides careful removal of water and organic impurities from the surface as well as ensures complete  $\text{O}_2$  oxidation of the iron not constituting  $\alpha$ -sites. The  $\text{O}_{\alpha}$  deposition was performed by  $\text{N}_2\text{O}$  decomposition at 230 °C (20 min) with initial pressure 0.6 Torr.

Procedures for the measurement of  $\text{O}_{\alpha}$  concentration are described in [29,43]. In the present work, we used mainly two methods based on (i) the amount of  $\text{N}_2$  evolved Eq. (1) and (ii) the equilibrium isotopic composition of dioxygen at the  $^{18}\text{O}_2/^{16}\text{O}_{\alpha}$  exchange. Both methods give close results and are not destructive, so that  $\alpha$ -oxygen can be used in further experiments with alkenes.  $\alpha$ -Oxygen concentration on the FeZSM-5 sample was  $6.0 \cdot 10^{19}$  sites/g (100  $\mu\text{mol/g}$ ), whereas on 0.2Na-FeZSM-5 and 0.4Na-FeZSM-5 samples, it was  $3.5 \cdot 10^{19}$  sites/g.

The reaction of  $\text{O}_{\alpha}$  with propylene and 1-butene was studied over the temperature range of  $-60$  to  $+25$  °C. A specified amount of alkene vapor was admitted into reaction volume at the closed reactor. The time of reactor opening served as the onset of reaction. Upon termination of the reaction, the sample was evacuated for 10 min with a gradual rise of temperature from  $-60$  to  $-20$  °C. Then sample was cooled to  $-60$  °C and subjected to extraction procedure. When the reaction was performed at 0 or 25 °C, the sample was evacuated at the temperature of experiment for 5 min and cooled to  $-60$  °C with subsequent extraction.

### 2.3. Infrared spectra

For recording the infrared (IR) spectra, the zeolite sample was placed in a specially designed IR reactor cell. The cell was made of quartz, which provides a convenient possibility for performing high temperature treatments of the sample up to 550 °C. The cell has a flange for connecting it with the vacuum setup to reproduce conditions of experiments conducted in the microreactor. After experiments, the reactor cell was sealed and transferred to the IR spectrometer.

IR spectra were recorded at room temperature on a Shimadzu 8300 Fourier spectrometer in the region of  $2200$ – $6000 \text{ cm}^{-1}$  at a resolution of  $4 \text{ cm}^{-1}$ . The region of lower frequencies was not informative because of a strong proper IR absorption of quartz. The spectra accumulated from 400 scans were converted from

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